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COMPRESSIBILITY OF NATURAL GAS AND ITS CONSTITUENTS WITH ANALYSES OF NATURAL GAS FROM 31 CITIES IN THE UNITED STATES

BY

G. A. BURRELL AND I. W. ROBERTSON

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COMPRESSIBILITY OF NATURAL GAS AND ITS CONSTITUENTS, WITH ANALYSES OF NATURAL GAS FROM 31 CITIES IN THE UNITED STATES.

By G. A. Burrell and I. W. Robertson.

INTRODUCTION.

As a continuation of the work described in a previous publication of the Bureau of Mines,[a] which presented the compressibility of the natural gas used in Pittsburgh, Pa., at pressures ranging from atmospheric up to 35.5 atmospheres, this paper shows the compressibility of three of the hydrocarbon gases (methane, ethane, and propane) that comprise natural gas, of carbon dioxide (another constituent of natural gas), and of natural gas from nine different cities. In addition, it contains analyses of natural gas from 31 cities and presents a formula by which the compressibility of any natural gas can be determined from the analysis. Data regarding other analyses, and the composition and characteristics of natural gas, are given in previous publications of the Bureau of Mines.[b]

From the results obtained by the ordinary combustion analysis of samples of natural gas the authors determined the compressibility of the samples collected in nine cities. The analyses of these samples are shown below:

TABLE 1.—*Analyses of samples of natural gas from nine cities in the United States.*

City.	Constituents.					Total.
	CO_2	CH_4	C_2H_6	N_2	H_2S	
Little Rock, Ark.	1.0	96.7	0.0	2.3	.....	100.0
Bartlesville, Okla.	2.8	89.1	4.2	3.9	.....	100.0
Cleveland, Ohio.	0.0	83.6	15.7	0.7	.....	100.0
Los Angeles, Cal.	25.1	59.1	14.5	1.3	.....	100.0
Palestine, Ill.	0.5	95.6	0.0	3.9	.....	100.0
Buffalo, N. Y.	0.0	88.1	11.5	0.4	.....	100.0
Kansas City, Mo.	0.8	84.1	6.7	8.4	.....	100.0
Charleston, W. Va.	0.0	76.8	22.5	0.7	.....	100.0
Olney, Ill.	0.0	37.5	59.6	1.7	1.2	100.0

[a] Burrell, G. A., and Robertson, I. W., The compressibility of natural gas at high pressures: Tech. Paper 131, Bureau of Mines, 1916, 12 pp.

[b] Burrell, G. A., and Seibert, F. M., The sampling and examination of mine gases and natural gas: Bull 42, Bureau of Mines, 1913, 116 pp. Burrell, G. A., Seibert, F. M., and Robertson, I. W., The analysis of natural gas and artificial illuminating gas by fractional distillation at low temperatures and pressures, Tech. Paper 104, 1915, 41 pp. Burrell, G. A., and Oberfell, G. G., The composition of the natural gas used in 25 cities: Tech. Paper 109, Bureau of Mines, 1915, 22 pp.

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PREPARATION OF PURE GASES.

The methods used in preparing pure gases for compressibility determinations were as follows: Methane, fractional distillation of natural gas at low temperatures and pressures; ethane, electrolysis of sodium acetate; propane, action of propyl iodide on a zinc-copper couple; carbon dioxide, action of sulphuric acid on a solution of potassium bicarbonate.

In preparing these gases extreme care was used to rid them of all impurities. In every case the final method of purification was fractional distillation at low temperatures and pressures.

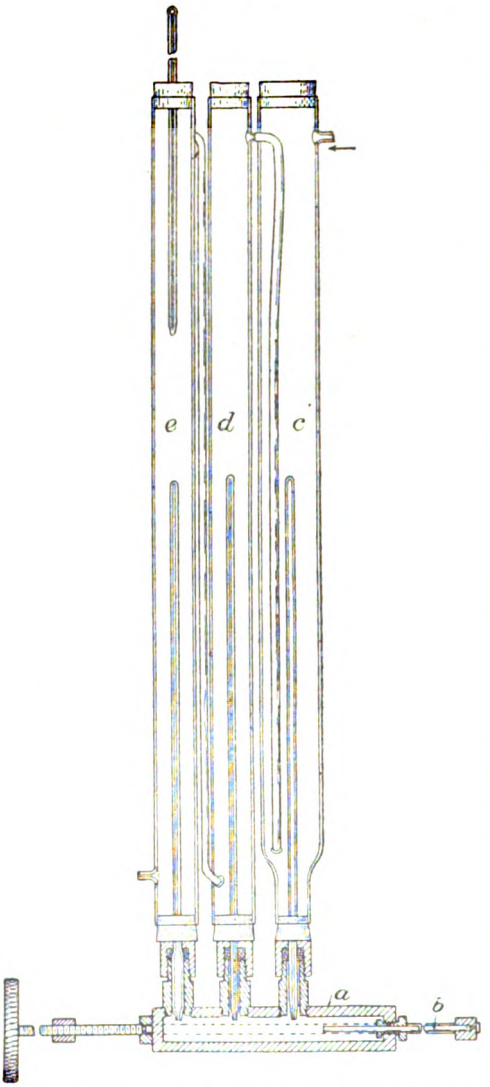

FIGURE 1.—Apparatus for determining compressibility of gas.

DETERMINATION OF COMPRESSIBILITY.

The apparatus with which the compressibility of the gases was determined is shown in figure 1. The three capillary tubes *e*, *d*, and *c*, passed through stuffing boxes into the chamber of the steel compression machine *a*. This chamber contained mercury, and by screwing the plunger *b* into the mercury, the latter could be forced into the glass capillary tubes, thereby compressing to the desired degree the gas contained therein. The capillary tube *c* contained the gas whose compressibility was measured. The tubes *d* and *e* contained pure air and served as air manometers (pressure gages.) The pressure-volume curve for air had been determined in previous experiments, reported in Technical Paper 131,[a] so that with any

[a] Burrell, G. A., and Robertson, J. W., The compressibility of natural gas at high pressures: Tech. Paper 131, Bureau of Mines, 1916, p. 8.

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position of the mercury in the tubes *d* and *e*, the pressure of the air could be determined. The gas in the tube *c* was always under the same pressure as the air in the tubes *d* and *e* plus or minus the difference in height of the mercury columns in the air manometer and gas manometer, therefore the pressure on the gas could be ascertained.

The glass capillary tubes *c*, *d*, and *e* were 0.8 mm. inside diameter with white backgrounds and were graduated as purchased. They were calibrated by means of the arrangement shown in figure 2. The capillary tube *e*, surrounded by a water jacket, *d*, fitted at the lower end into a small screw plunger, *a*, containing mercury and at the upper end it bent into a small porcelain capsule, *b*, that contained mercury. To calibrate the capillary tube, a small amount of weighed mercury was placed in *b* and a thread of it, *c*, was drawn into the tube by manipulating the screw plunger *a*. The remaining mercury in *b* was next weighed and the loss in weight from the original weight gave the weight of the small column of mercury *c*. This small column was then moved by means of the plunger *a* along the tube *e* and the volume of the latter calculated from the weight of the mercury thread.

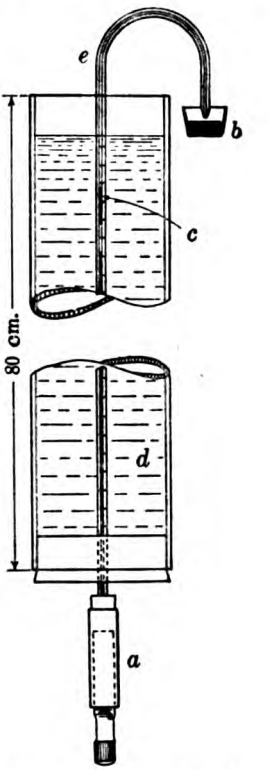

FIGURE 2.—Arrangement for calibrating capillary tube.

The compressibility of the gases was determined at a temperature of about 15° C. (59° F.). Water in the water jackets *e*, *d*, and *c* of the compression machine, figure 1, was kept at a constant temperature by passing it through the vessel *a*, figure 3. Tap water of a lower temperature than 15° C. was forced into the Wolff bottle *b* at *e* (see fig. 3). Thence it passed into a 5-gallon vessel *a* that was warmed with a Bunsen flame so as to keep it at a temperature of 15° C. The water next passed into the water jacket of the compression machine. No trouble was experienced in keeping the temperature within ±0.3° of 15° C. during a determination that lasted not longer than one hour.

The compressibility data for the natural gas used in Buffalo, N. Y., are shown in the following table, which gives the volume of the gas, the pressure corresponding to the volume, the product of the pressure and volume, and the deviation from a perfect gas (volume varying with pressure according to Boyle's law). Similar data were obtained for all the gases whose compressibility was determined.

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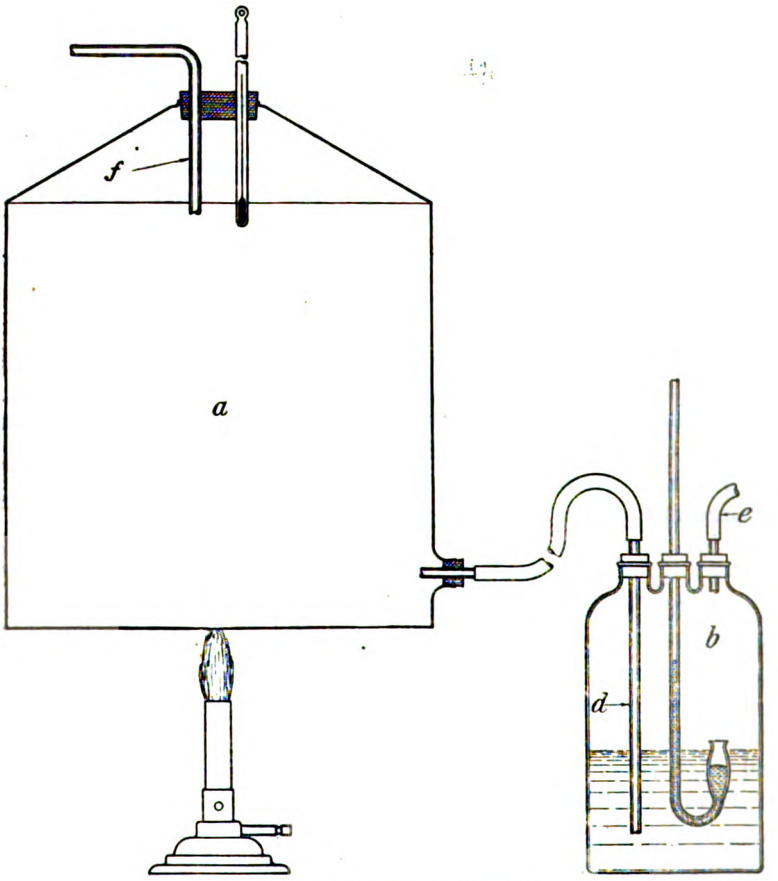

FIGURE 3.—Constant-temperature bath.

TABLE 2.—*Compressibility data for natural gas used in Buffalo, N. Y.*

Volume of gas (c. c.).	Pressure of gas (atmospheres).	Product of pressure and volume (PV).	Deviation from perfect gas.[a]	Volume of gas (c. c.).	Pressure of gas (atmospheres).	Product of pressure and volume (PV).	Deviation from perfect gas.[a]
0.48540	1.32	0.6407	99.6	0.02854	21.25	0.6064	93.5
.40180	1.61	.6469	99.1	.02557	23.55	.6022	92.6
.28690	2.22	.6369	99.0	.02264	26.45	.5988	91.8
.20150	3.04	.6347	98.4	.02138	27.83	.5950	91.3
.12030	5.25	.6315	97.8	.01904	31.09	.5919	90.8
.10430	6.04	.6297	97.5	.01843	32.04	.5904	90.7
.08860	7.08	.6275	97.2	.01721	34.12	.5872	89.9
.07640	8.20	.6267	97.1	.01635	35.86	.5863	89.5
.06420	9.73	.6247	96.7	.01573	37.13	.5840	89.2
.05232	11.91	.6231	96.2	.01483	39.21	.5815	88.7
.04630	13.38	.6200	95.6	.01449	39.94	.5787	88.3
.04043	15.26	.6170	95.1	.01420	40.71	.5781	88.2
.03450	17.76	.6127	94.4	.01393	41.52	.5779	88.1
.03151	19.35	.6097	93.9	.01366	42.19	.5763	87.7

[a] On the basis of a perfect gas being rated as 100.

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The data shown in figures 4, 5, 6, and 7 give the results of measuring the compressibility of the natural gas used in nine different cities and of several pure gases that are found in natural gas. The compressibility of these pure gases was determined so one could after making a simple analysis of a given natural gas determine its compressibility by referring to these curves. The procedure would be as follows:

DEVIATION OF FORMULA FOR COMPRESSIBILITY.

The natural gas used in Buffalo is composed of 88.1 per cent CH_4, 11.5 per cent C_2H_6 and 0.4 per cent N_2. Suppose it is desired to determine the compressibility of this gas at a pressure of 40 atmospheres

(1) The partial pressures of the three constituents are:

$CH_4 = 0.881 \times 40 = 35.2 = P_1$
$C_2H_6 = 0.115 \times 40 = 4.6 = P_2$
$N_2 = 0.004 \times 40 = 0.2 = P_3$

(2) According to the compressibility curves in figure 7 the deviations per atmosphere for methane, ethane, propane, and carbon dioxide are:

$CH_4 = a = 0.228$ per cent
$C_2H_6 = b = 0.90$ per cent
$C_3H_8 = c = 1.9$ per cent
$CO_2 = d = 0.67$ per cent

and the values for nitrogen and air are:

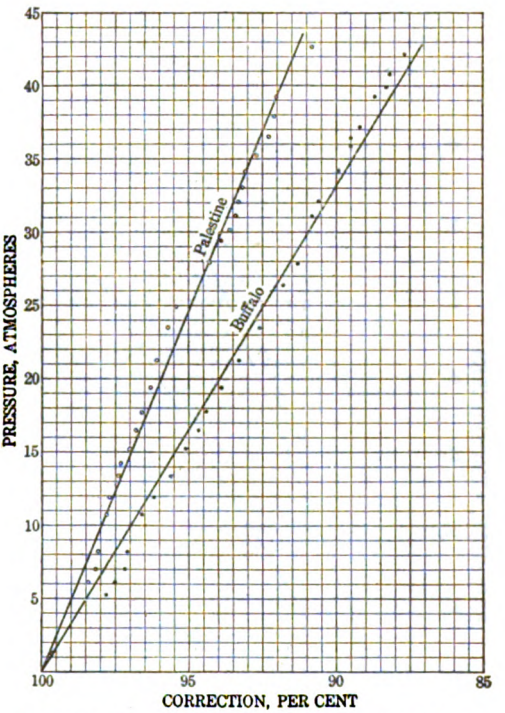

FIGURE 4.—Compressibility curves of natural gas from Palestine, Ill., and Buffalo, N. Y.

$N_2 = e = 0.01$ per cent
Air $= f = 0.05$ per cent

(3) The formula for the total deviation thus becomes:

$$D = aP_1 + bP_2 + cP_3 + dP_4 + \text{etc.}$$

Substituting values of (1) and (2) in (3)

$D = (0.228 \times 35.2) + (0.90 \times 4.6) = 8.03 + 4.14 = 12.17$ per cent, or 87.83 on the basis of an ideal gas being 100.

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The calculated and the determined deviations at a pressure of 20 atmospheres are shown in the following table for the different samples of natural gas whose compressibility was determined by the authors.

Calculated and determined compressibility of natural gas at a pressure of 20 atmospheres, from nine cities.

City.	Observed deviation.	Calculated deviation.
Little Rock, Ark	94.2	95.6
Palestine, Ill	95.8	95.6
Kansas City, Mo	96.0	95.6
Cleveland, Ohio	95.7	95.5
Bartlesville, Okla	95.2	95.2
Buffalo, N. Y	94.0	93.9
Charleston, W. Va	93.6	92.5
Los Angeles, Cal	92.2	91.4
Olney, Ill	87.7	87.6

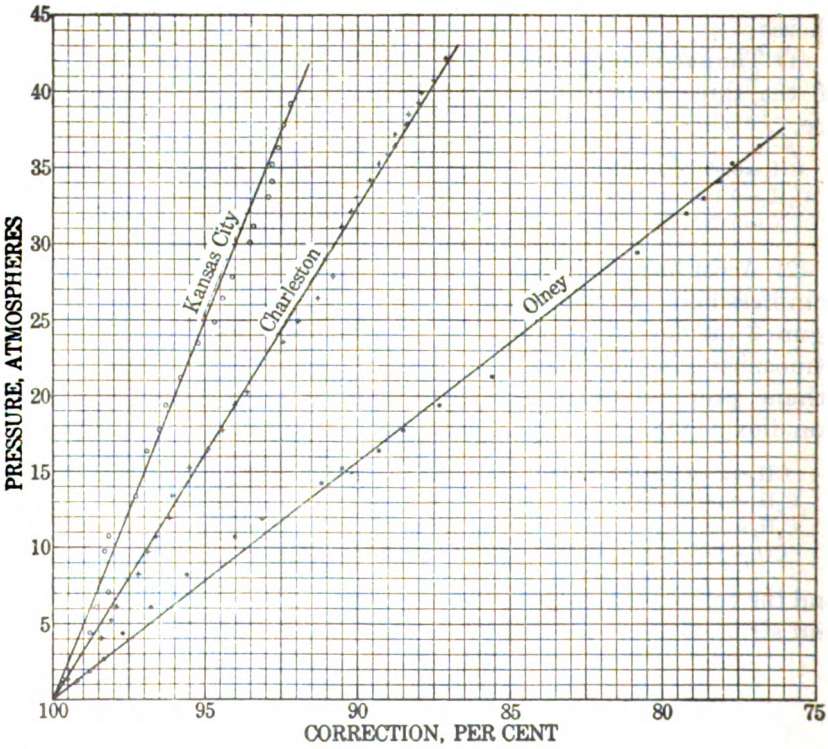

FIGURE 5.—Compressibility curves of natural gas from Kansas City, Mo., Charleston, W. Va. and Olney, Ill.

The results show that it is possible to calculate the compressibility of natural gas from different sources, provided an ordinary analysis of the natural gas has been made. This is important because the direct determination of compressibility is a tedious and somewhat difficult operation.

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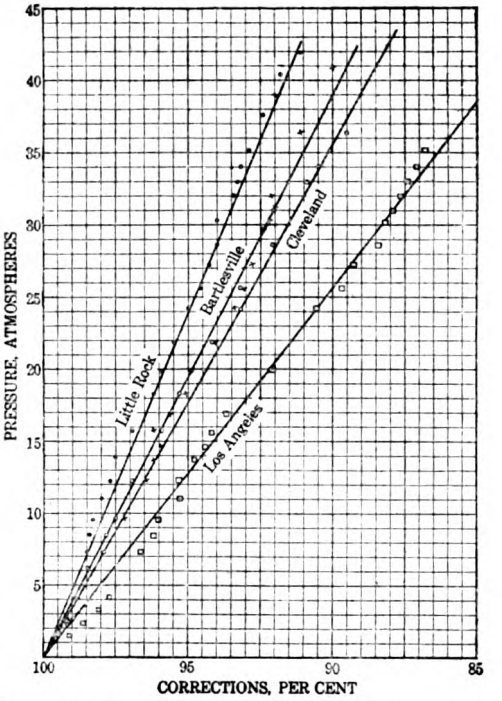

FIGURE 6.—Compressibility curves of natural gas from Little Rock, Ark., Bartlesville, Okla., Cleveland, Ohio, and Los Angeles, Cal.

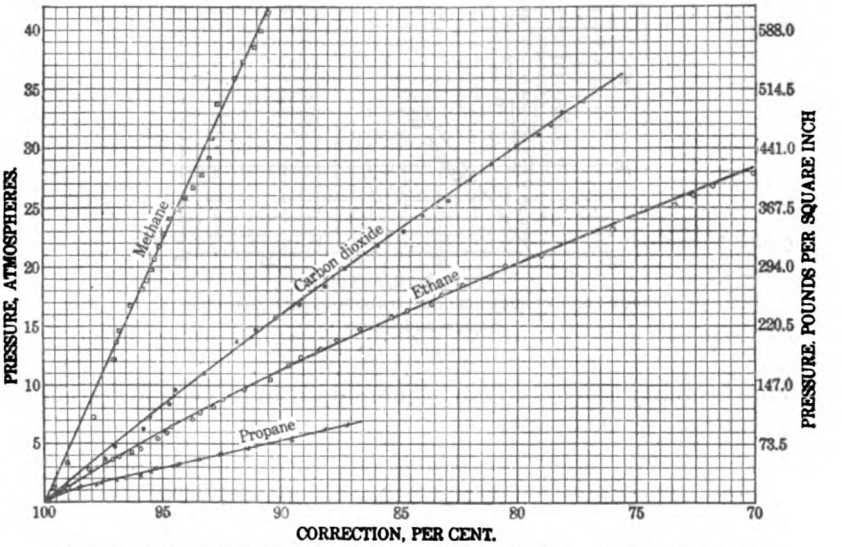

FIGURE 7.—Compressibility curves of methane, carbon dioxide, ethane, and propane.

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WORK OF AMAGAT AND OMNES.

Of interest in this connection is the work of E. H. Amagat [a] on the compressibility of air, methane, ethylene, carbon dioxide, and carbon monoxide, and of Kamerlingh-Omnes [b] on helium.

Curves showing the results of the work of Amagat and Omnes are given in figures 8 and 9, wherein the solid lines represent the range

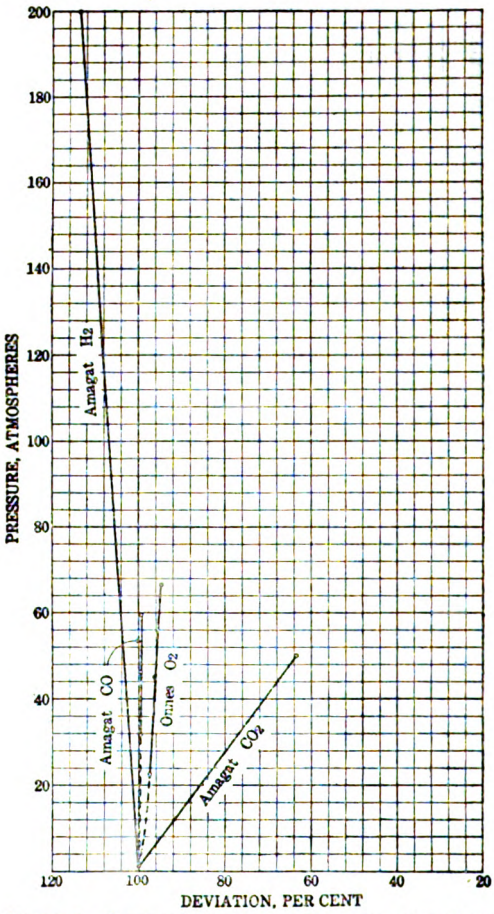

FIGURE 8.—Compressibility curves of three gases, according to Amagat and Omnes.

of compressibility they studied. The dotted lines were extrapolated by the authors of this paper.

Amagat's work on carbon dioxide corresponds fairly closely with the work of the authors on that gas. At 30 atmospheres pressure the authors found a deviation of 20 per cent from an ideal gas, whereas

[a] Landolt and Bornstein, Physikalisch chemische Tabellen, 4th ed., pp. 64, 65, 66.
[b] Same, p. 63.

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Amagat found 21 per cent. For methane Amagat found a deviation of 9 per cent at 40 atmospheres (by extrapolation), which is the same as the authors found.

COMPOSITION OF NATURAL GAS.

The results of the examination of samples of natural gas collected in 31 cities in the United States other than the cities named in Tech-

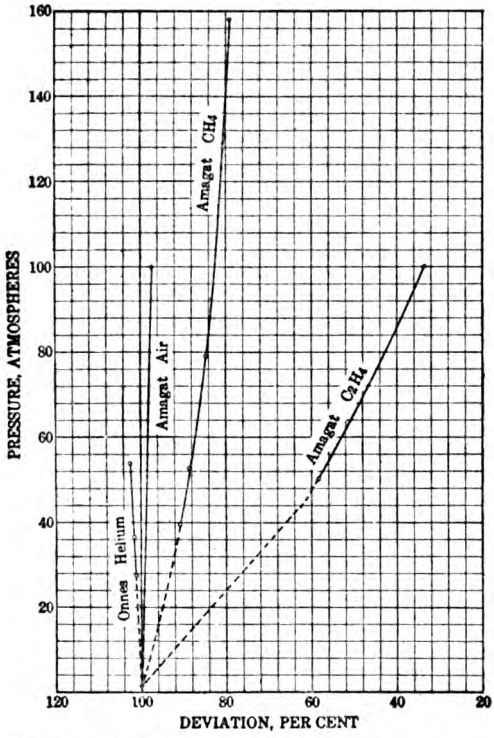

FIGURE 9.—Compressibility curves of air and of three gases, according to Amagat and Onnes.

nical Paper 109[a] are given in the following table. Methods of analysis and various properties of natural gas are discussed in that paper.

By means of the formula given on page 9, the compressibility of each natural gas in the table can be determined from the analysis.

[a] Burrell, G. A., and Oberfell, G. G., The composition of the natural gas used in 25 cities, with a discussion of the properties of natural gas: Tech. Paper 109, Bureau of Mines, 1913, 22 pp.

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TABLE 3.—*Analyses of natural gas collected in 31 cities in the United States.*

Laboratory No.	State.	County.	Town.	Paraffin hydrocarbons (C_nH_{2n+2}).	Methane (CH_4).	Ethane (C_2H_6).	Carbon dioxide (CO_2).	Nitrogen (N_2).	Calculated gross heating value, B. t. u. per cubic foot (760 mm. pressure).		Calculated specific gravity (air=1).
									0° C.	60° F.	
7176	Ala.	Fayette	Fayette	97.6	97.6	0.0	0.3	2.10	1,039	983	0.57
7309	Ark.	Crawford	Alma	99.2	99.2	0.0	.20	.6	1,057	1,000	.56
6888	...do.	Pulaski	Little Rock	96.7	96.7	0.0	1.00	2.3	1,030	974	.57
7341	Cal.	Los Angeles	Los Angeles	93.5	77.5	16.0	6.50	0.0	1,123	1,062	.70
7359	...do.	...do.	...do.	73.1	59.2	13.9	26.20	.7	889	841	.88
7340	...do.	...do.	...do.	98.0	70.0	28.0	1.10	.9	1,267	1,199	.71
7029	Ill.	Lawrence	Olney	97.1	37.5	59.6	0.0	[a]1.7	1,591	1,505	.86
6857	...do.	Crawford	Palestine	95.6	95.6	0.0	.5	3.9	1,018	963	.58
7147	Ind.	Adams	Geneva	98.8	75.4	23.4	0.0	1.2	1,238	1,171	.68
7280	Kans.	Montgomery	Coffeyville	98.0	98.0	0.0	1.2	.8	1,044	988	.57
7148	...do.	Crawford	Pittsburg	93.0	90.5	2.5	.4	6.6	1,010	955	.60
7173	Ky.	Boyd	Ashland	79.0	75.0	24.0	.0	1.0	1,245	1,178	.68
7265	...do.	Fayette	Lexington	99.0	76.4	22.6	.0	1.0	1,234	1,167	.67
6847	Mo.	Jackson	Kansas City	90.8	84.1	6.7	.8	8.4	1,025	965	.63
7233	N. Y.	Chenango	Elmira	99.0	84.0	15.0	.0	1.0	1,174	1,111	.63
7240	...do.	Allegany	Bolivar	97.4	59.8	37.6	.4	2.2	1,336	1,264	.75
6853	...do.	Erie	Buffalo	99.6	88.1	11.5	.0	.4	1,152	1,090	.61
6856	...do.	Genesee	Pavilion	98.7	91.9	6.8	.0	1.3	1,105	1,045	.59
6817	...do.	Allegany	Wellsville	98.0	78.1	19.9	.0	2.0	1,202	1,137	.65
7151	Ohio.	Ashtabula	Ashtabula	98.7	82.2	16.5	.0	1.3	1,182	1,118	.65
7357	...do.	Allen	Lima	96.3	83.5	12.8	.0	3.7	1,127	1,066	.63
7169	...do.	Miami	Piqua	90.9	78.3	12.6	.2	8.9	1,068	1,010	.66
7171	...do.	Erie	Sandusky	96.0	83.5	12.5	.2	3.8	1,122	1,061	.63
7266	...do.	Licking	Utica	93.9	74.8	19.1	.3	5.8	1,152	1,090	.68
7279	Okla.	Logan	Guthrie	91.9	73.5	18.4	.0	8.1	1,125	1,064	.68
7277	...do.	Creek	Sapulpa	98.8	93.1	5.7	.4	.8	1,098	1,039	.59
7181	Pa.	Blair	Altoona	99.0	90.0	9.0	.2	.8	1,126	1,065	.60
6815	...do.	Venango	Oil City	97.7	64.3	33.4	.0	3.3	1,306	1,235	.74
7353	...do.	McKean	St. Marys	99.2	88.0	11.2	.0	.8	1,146	1,084	.61
7167	...do.	...do.	Sharon	99.3	32.3	67.0	.0	.7	1,591	1,505	.89
6845	W. Va.	Kanawha	Charleston	99.3	76.8	22.5	.0	.7	1,236	1,169	.67
7384	...do.	Harrison	Clarksburg	99.3	66.6	32.7	.0	.7	1,318	1,247	.72
7175	...do.	Marion	Fairmont	99.0	82.0	17.0	.1	.9	1,189	1,125	.64

[a] Contained also 1.2 per cent hydrogen sulphide (H_2S.)

NOTE.—The sum of the methane, ethane, carbon dioxide and nitrogen totals 100 per cent.

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